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EFFECT OF HEAT TREATMENT AND INHIBITOR ON CORROSION BEHAVIOR OF AISI 4140 STEEL

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ABSTRACT

Heat treatment effect on corrosion behavior of AISI 4140 steel and thiourea inhibition action on corrosion of AISI 4140 steel in as bought as well as heat-treated conditions such as annealing, normalizing, hardening and tempering in 1N HCl solution at room temperature was investigated using potentiostatic polarization technique. Results shows that heat treatment has negligible effect on the corrosion behaviour of steel in comparison with the as bought specimen. Different concentrations of thiourea are used in 1N HCl solution. Inhibition efficiency of thiourea is concentration dependent. Inhibition efficiency increases with a increase in concentration up to a critical concentration. Thermodynamic studies have confirmed that adsorption of inhibitor adopted Temkins ' adsorption isotherm and physisorption process controls the inhibition.

KEYWORDS: Corrosion, Heat Treatment, AISI 4140 Steel, Thiourea, Adsorption Isotherm & Inhibition Efficiency

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Original Article

1. INTRODUCTION

Heat treatment is one of the ways to alter the structure of the material to obtain the required properties. Annealing, normalizing, hardening and tempering heat treatments are used to alter the microstructure and mechanical properties of materials, particularly steels. Annealing is a form of heat treatment used to soften iron or steel materials and refine its grains. Because of the microstructure of ferrite-pearlite; it is used where elongation and a considerable amount of tensile strength are needed in the materials. The material is heated to the austenitic temperature range during normalization and air cooled. This is done in order to have a pearlite structure that results in greater strength and hardness than the sample purchased. In the hardening process, the steel or its alloy is heated to a temperature sufficiently high to allow austenite formation, held for a certain time at that temperature, and then quenched in oil or water. Tempering is done to give the hardened sample ductility and hardness. Heat treatment is well known to cause changes in metal microstructures such as changes in phase, grain size, residual stress and crack [1-2].

Steel corrosion was seen as a major industrial problem, costing hundreds of billions of dollars, due to its environmental and economic effects. This problem has been investigated by scientists from different fields to minimize its adverse effects and many methods of prevention has been reported. One of the most effective

solutions to this problem, especially in acidic environments, is the use of organic compounds as corrosion inhibitors [3]. In science and technology, corrosion is a prevalent damaging phenomenon. Iron and steel, due to their affordability, low price, simple manufacturing and high strength, are the most commonly used products in the production of oil field operating platforms. Many industrial media generally have an abundance of elemental gases, inorganic salts and acidic solutions that mostly impact corrosion process levels. Exposures can be extreme to the properties of materials, resulting in a sudden loss of the component in use. Therefore, to have an increased service life, it is necessary to increase the corrosion resistance of metals. The amount of corrodent and the processing time influences the metal corrosion. With rising concentration of corrosive media and exposure time, the risk of metal dissolution increases. In all the acidic media analyzed, corrosion levels of mild steel were found to be higher than those of high carbon steels. This could be certified by the fact that the carbon content has little or no effect on the general resistance of steels to corrosion [4].

Double-phase steel's poor corrosion resistance compared to stainless steel limits the former's use in the automotive industry, particularly in automotive exterior panels [5]. Many mineral acid solutions are used to a large degree for various treatments of industrial materials such as pickling, descaling, acid cleaning, and oil-well acidizing. So the use of corrosion inhibitors is very important to keep the steel surface intact and reduce its corrosion rate. Corrosion occurs when a metal gives its electrons to the oxidizing substances. This can be postponed by painting the metal, or use corrosion inhibitors to protect these metals from corrosion. Many of the well-known inhibitors are organic compounds that contain atoms of nitrogen, sulfur and oxygen [6-9].

Corrosion inhibitors bind to the metal / metal oxide layer (e.g., by chemisorption, physisorption, complexation, or precipitation) and prevent oxygen from reaching the cathode. This inturn prevents hydrogen from being spread from the cathode or inhibits metal dissolution by anodic inhibitors. When added in small quantities to the medium, inhibitors restrict or prevent the reaction between a metal and its environment. The use of inhibitors is one of the most effective methods of defense against corrosion, especially in the extraction and processing of oil, gas and other chemical and petrochemical industries, heavy industrial development, water treatment plants, water containers, water-containing hydraulic fluids, engine coolants, ferrous metal cleaners, automatic transmission fluids, automotive component manufacture, cutting fluids etc. Metal salts that have a passive effect and metal reaction are inorganic inhibitors. Many carbon steel synthetic compounds can reduce the damage of corrosion [10–12].

Table 1. AISI 4140 steel chemical composition used in this work.

Fe	C	Si	Mn	Cr	P	Mo	S
97.56%	0.38%	0.16%	0.8%	1.00%	0.035%	0.02%	0.04%

2. EXPERIMENTAL DETAILS

2.1 Specimen Preparation

Chemical composition of the material used for present study is shown in Table 1. Standard specimens are prepared with the required dimensions for corrosion test as per the ASTM standard. Fig. 1 shows the specimen used for corrosion test.

Figure 1: Specimen for Corrosion Test.

2.2 Heat Treatment Procedure

Using electric furnace, specimens are heated to the austenitic state. All specimens are prepared from purchased steel and are subjected to four types of heat treatments such as annealing, normalizing, hardening, tempering and compared to the specimen purchased. Five sets of specimens are being prepared for five conditions. Except tempering and as bought specimen, rest are kept in the furnace and heated until the temperature reaches 900^0C, in order to convert the room temperature structure into austenite. The furnace temperature is then maintained at 900^0C for one hour. A set of specimen is removed and cooled outdoors to normalize. The specimens are removed to harden and quickly quenched in oil. In the furnace itself, the set of specimens is left to cool to anneal. For tempering, the set of specimens are heated to 900^0C and kept for an hour at that temperature, then quickly quenched in oil. It is then heated again to 500^0C, held for about 2 hours at that temperature, then removed from the furnace and subjected to air cooling. All the specimens are cleaned by using emery paper. Used quechant is SAE 30 oil.

2.3 Testing

The heat treated specimens are further subjected to corrosion test in the presence and absence of inhibitor. Thiourea is used as inhibitor. Inhibitor is the compound used to protect the material from corrosion. Thiourea is an organic compound of carbon, nitrogen, sulfur and hydrogen, with the formula CSN_2H_4 or $(NH_2)_2CS$.

In this experiment the inhibition effect of Thiourea on the corrosion of heat treated as well as as bought AISI 4140 steel specimens in hydrochloride acid medium is analyzed. Test is carried out at room temperature and concentration of acid used is 1N. Five different concentrations (50, 100, 150, 200 and 250ppm) of inhibitor is used to determine maximum efficiency of inhibitor. The specimen was polished after each experiment to provide constant conditions for the specimen during the whole test series. Tafel Extrapolation Technique is used to determine the corrosion current density, corrosion potential, corrosion rate and inhibitor efficiency.

3. RESULTS AND DISCUSSIONS

Inhibition effect of thiourea on AISI 4140 steel in 1N HCl solution at room temperature has been investigated by using potentiostatic polarization method. It is observed from polarization plots that there is negligible shift in corrosion potential (E_{corr}) indicating that thiourea acts as mixed type of inhibitor in the heat treated (annealed, normalized, hardened and tempered) as well as in as bought conditions. It is also observed from the results that there is a substantial reduction in corrosion current density (I_{corr}) in the presence of thiourea. Inhibition Efficiency (IE) of the compound increases with aincrease in inhibitor concentration up to a critical concentration (200 ppm) in as bought as well as heat treated AISI 4140 steel.

- From the test, it is evident that the heat treatment of AISI 4140 steel's corrosion behavior compared to as purchased has no / negligible effect at room temperature in 1N HCl solution. It is also apparent from the findings that an improvement in thiourea concentration has a significant impact on Inhibition Efficiency (IE), suggesting that the IE of the compound being tested is the concentration dependent on both as purchased and heat treated conditions in 1N HCl solution.
- The difference in the Corrosion Rate (CR) with the concentration of inhibitors (Figure 7) indicates that the corrosion level of steel decreases with a increase in thiourea concentration to a critical concentration (200 ppm) and a further rise in concentration raises the rate of corrosion. This may be due to the desorption of steel surface blocker molecules.
- The inhibitor efficiency variance with concentration of inhibitors (Figure 8) shows that steel inhibition efficiency improves with a increase in thiourea concentration up to a critical concentration (200 ppm) and further increase in concentration reduces inhibitor efficiency.

Mathematic expression used for determining CR and IE are

$$CR= \frac{0.129 \times \text{Equivalent weight} \times \text{Icorr}}{\text{Density}}$$

$$IE(\%) = \frac{\text{Icorr} - \text{Icorr(inh)}}{\text{Icorr}} \times 100$$

Where

I_{corr} ---------------------Corrosion Current Density in μA/cm^2

$I_{corr(inh)}$ ----------------Corrosion current density in the presence of inhibitor

Specimen Diameter-- 11.2mm

Specimen Area Exposed to Corrosion-------------- 1cm^2

Table 2: Tafel Extrapolation Outcomes for Corrosion Inhibition of AISI 4140 Steel as Bought Sample in 1N HCl at various Thiourea Concentrations at Room Temperature.

Concentration (ppm)	OCP (mV)	E_{corr} (mV)	I_{corr} ($\mu A/cm^2$)	Corrosion rate (mpy)	Efficiency (%)
Blank	-490	-495	600	274.69	-------
50	-510	-500	300	137.34	50.00
100	-510	-500	280	128.19	53.30
150	-510	-500	259	118.57	56.83
200	-500	-495	230	105.30	61.67
250	-490	-485	260	119.03	56.67

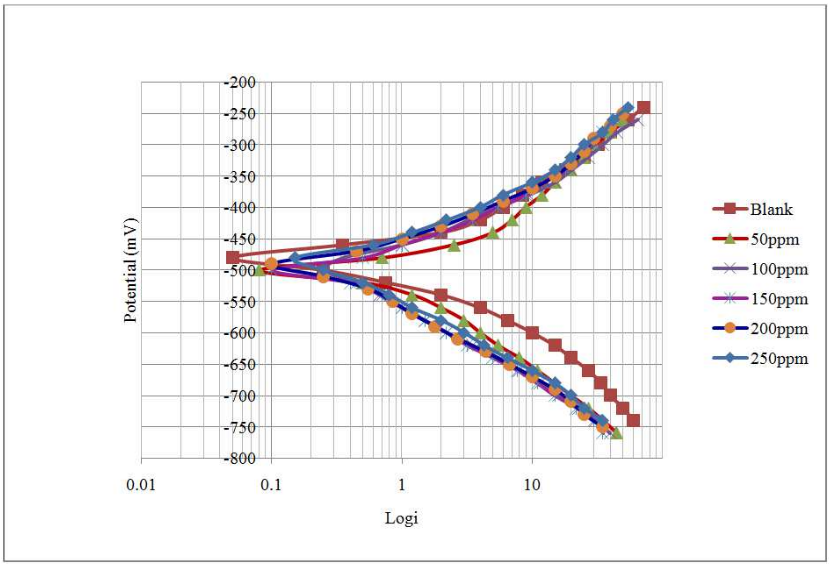

Figure 2: Tafel Extrapolation Curves for as Bought Specimen of AISI 4140 Steel in 1N HCl at Room Temperature in the Absence and Presence of Thiourea.

Table 3: Tafel Extrapolation Outcomes for Corrosion Inhibition of AISI 4140 Steel Annealed Sample in 1N HCl at Various Thiourea Concentrations at Room Temperature

Concentration (ppm)	OCP (mV)	E_{corr} (mV)	I_{corr} ($\mu A/cm^2$)	Corrosion rate (mpy)	Efficiency (%)
Blank	-530	-510	680	311.31	--------
50	-520	-510	390	178.55	42.65
100	-520	-515	360	164.81	47.05
150	-520	-510	330	151.07	51.47
200	-510	-505	300	137.34	55.88
250	-500	-508	332	151.99	51.18

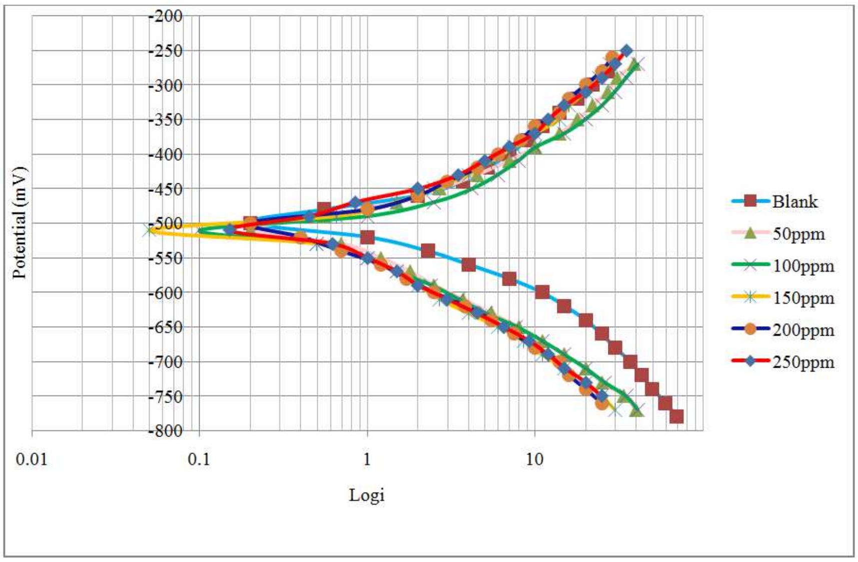

Figure 3: Tafel Extrapolation Curves for Annealed Specimen of AISI 4140 Steel in 1N HCl at Room Temperature in the Absence and Presence of THIOUREA.

Table 4: Tafel Extrapolation Outcomes for Corrosion Inhibition of AISI 4140 Steel Normalized Sample in 1N HCl at Various Thiourea Concentrations at Room Temperature.

Concentration (ppm)	OCP (mV)	E_{corr} (mV)	I_{corr} ($\mu A/cm^2$)	Corrosion rate (mpy)	Efficiency (%)
Blank	-520	-505	610	279.26	--------
50	-500	-505	340	155.66	44.26
100	-510	-510	300	137.34	50.82
150	-510	-498	280	128.19	54.09
200	-510	-500	220	100.72	58.19
250	-510	-500	266	121.77	55.41

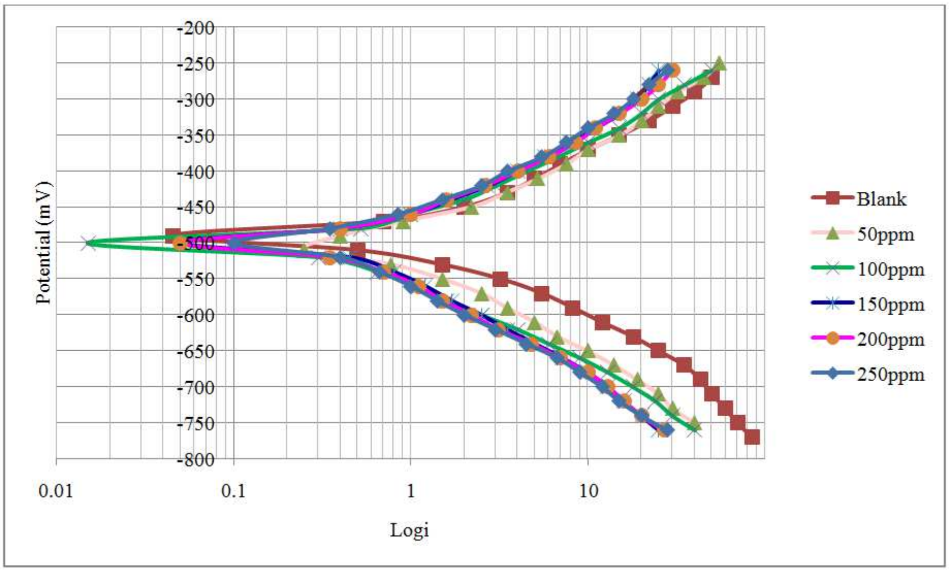

Figure 4: Tafel Extrapolation Curves for Normalized Specimen of AISI 4140 Steel in 1N HCl at Room Temperature in the Absence and Presence of Thiourea.

Table 5: Tafel Extrapolation Outcomes for Corrosion Inhibition of AISI 4140 Steel Hardened Sample in 1N HCl at Various Thiourea Concentrations at Room Temperature.

Concentration (ppm)	OCP (mV)	E_{corr} (mV)	I_{corr} ($\mu A/cm^2$)	Corrosion Rate (mpy)	Efficiency (%)
Blank	-530	-515	620	283.84	--------
50	-510	-508	290	132.77	53.23
100	-510	-505	270	123.61	56.45
150	-510	-509	240	109.87	61.29
200	-490	-507	210	96.14	66.13
250	-510	-510	244	111.71	60.61

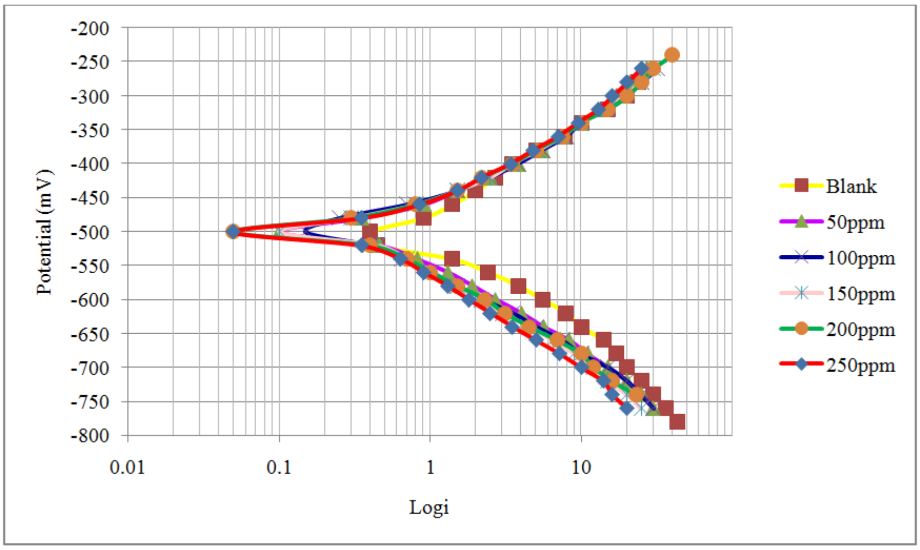

Figure 5: Tafel Extrapolation Curves for Hardened Specimen of AISI 4140 Steel in 1N HCl at Room Temperature in the Absence and Presence of Thiourea.

Table 6: Tafel Extrapolation Outcomes for Corrosion Inhibition of AISI 4140 Steel Tempered Sample in 1N HCl at Various Thiourea Concentrations at Room Temperature.

Concentration (ppm)	OCP (mV)	E_{corr} (mV)	I_{corr} ($\mu A/cm^2$)	Corrosion rate (mpy)	Efficiency (%)
Blank	-530	-515	770	352.51	--------
50	-520	-515	460	210.59	40.26
100	-520	-520	410	187.70	46.75
150	-520	-522	370	169.39	51.95
200	-520	-518	337	154.28	56.23
250	-510	-510	377	172.59	51.04

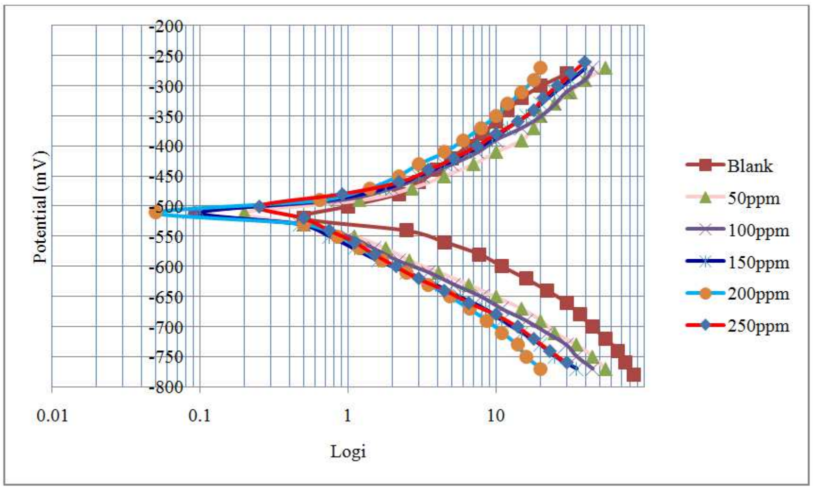

Figure 6: Tafel Extrapolation Curves for Tempered Specimen of AISI 4140 Steel in 1N HCl at Room Temperature in the Absence and Presence of Thiourea.

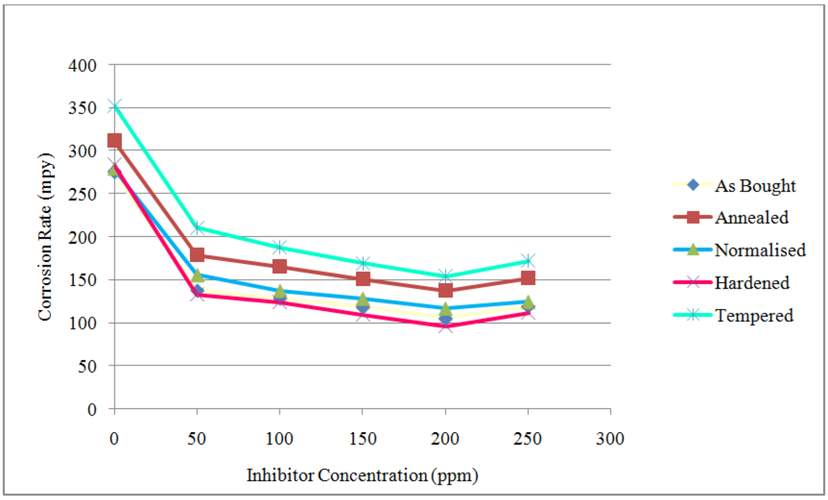

Figure 7: Variation of Corrosion Rate with Inhibitor Concentration of AISI 4140 Steel in as Bought as Well as Heat Treated Conditions in 1N HCl at Room Temperature.

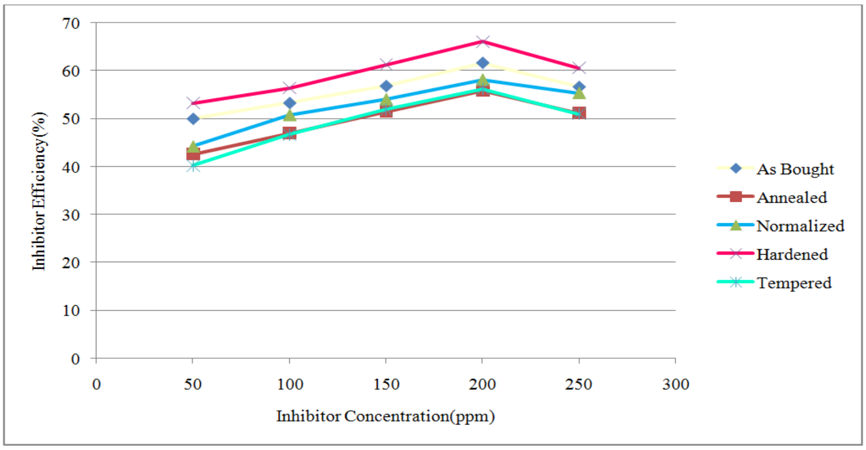

Figure 8: Variation of Inhibition Efficiency with Inhibitor Concentration of AISI 4140 Steel in as Bought as well as Heat Treated Conditions in 1N HCl at Room Temperature.

3.1 Free Energy of Adsorption

Free energy of adsorption is calculated using the relationship

$-\Delta G_{ads} = R\times T\times \ln(55.5K)$ Where $K = \frac{\theta}{C(1-\theta)}$

ΔG_{ads} = Gibbs free energy of adsorption

K= Equilibrium constant

θ = Degree of surface coverage

C = Concentration of inhibitor in moles

T= Temperature in Kelvin

R= Universal gas constant

55.5= Concentration of water in $molL^{-1}$

From the (Table 7–Table 11) it is observed that the negative values of ΔG_{ads} suggest spontaneous adsorption and heavy interaction of the inhibitor molecules on the AISI 4140 steel surface. Since the values of the ΔG_{ads} obtained are less than 40KJmol^{-1}, physisorption mechanism is used to adsorb inhibitor molecules on the steel surface of the AISI 4140. Mechanism of physisorption implies the film formation on the steel surface of adsorptive material.

Table 7: Gibbs Free Adsorption Energy of as Bought AISI 4140 Steel Sample in 1N HCl at Various Thiourea Concentrations at Room Temperature.

Concentration (ppm)	Surface Coverage (θ)	$-\Delta G_{ads}$ (KJmol^{-1})
50	0.5	28.68
100	0.53	27.23
150	0.56	26.51
200	0.61	26.31
250	0.56	25.22

Table 8: Gibbs Free Adsorption Energy of Annealed AISI 4140 Steel Sample in 1N HCl at Various Thiourea Concentrations at Room Temperature.

Concentration (ppm)	Surface Coverage (θ)	$-\Delta G_{ads}$ (KJmol^{-1})
50	0.42	27.86
100	0.47	26.62
150	0.51	26.00
200	0.55	25.68
250	0.51	24.71

Table 9: Gibbs Free Adsorption Energy of Normalized AISI 4140 Steel Sample in 1N HCl at Various Thiourea Concentrations at Room Temperature.

Concentration (ppm)	Surface Coverage (θ)	$-\Delta G_{ads}$ (KJmol^{-1})
50	0.44	28.07
100	0.51	27.03
150	0.54	26.30
200	0.58	25.99
250	0.55	25.11

Table 10: Gibbs Free Adsorption Energy of Hardened AISI 4140 Steel Sample in 1N HCl at Various Thiourea Concentrations at Room Temperature.

Concentration (ppm)	Surface Coverage (θ)	$-\Delta G_{ads}$ (KJmol^{-1})
50	0.53	28.98
100	0.56	27.54
150	0.61	27.03
200	0.66	26.85
250	0.6	25.63

Table 11: Gibbs Free Adsorption Energy of Tempered AISI 4140 Steel Sample in 1N HCl at Various Thiourea Concentrations at Room Temperature.

Concentration (ppm)	Surface Coverage (θ)	$-\Delta G_{ads}$ (KJmol^{-1})
50	0.4	27.65
100	0.46	26.52
150	0.52	26.10
200	0.56	25.79
250	0.51	24.71

3.2 Mechanism of Corrosion Inhibition

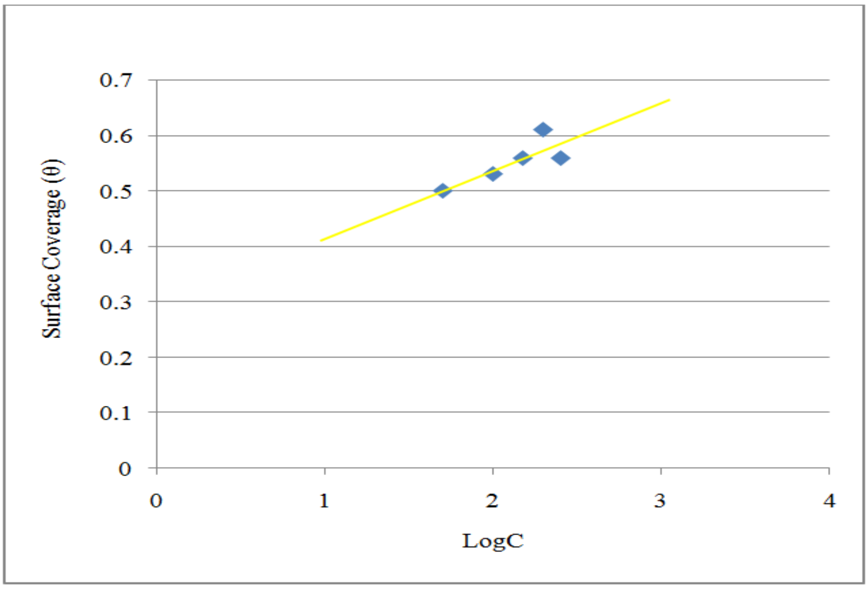

Figure 9: Curve Fitting of Temkins' Adsorption Isotherm for as Bought Specimen of AISI 4140 Steel in 1N HCl at Room Temperature.

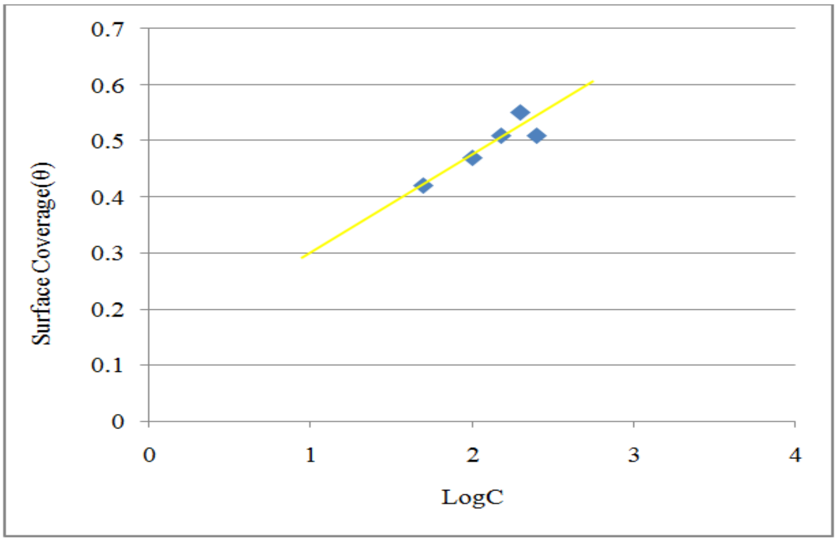

Figure 10: Curve Fitting of Temkins' Adsorption Isotherm for Annealed Specimen of AISI 4140 Steel in 1N HCl at Room Temperature.

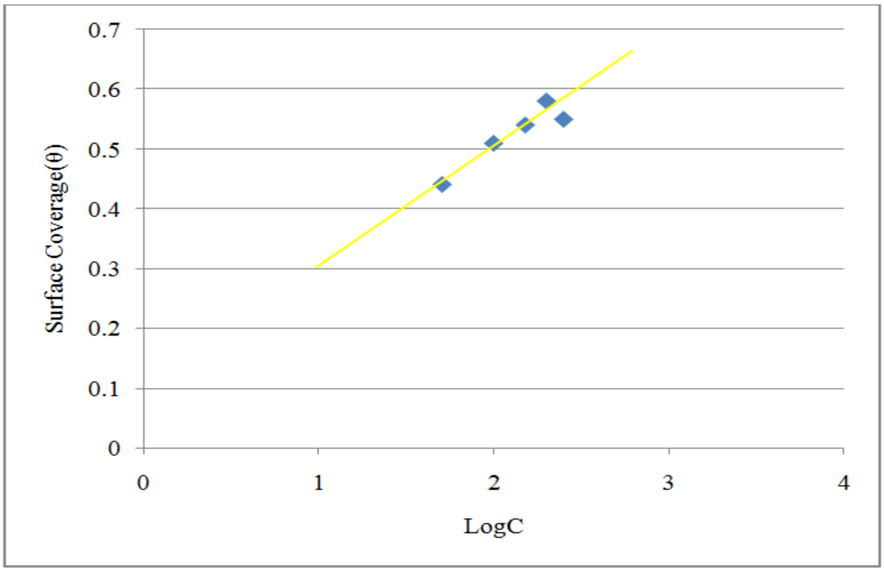

Figure 11: Curve Fitting of Temkins' Adsorption Isotherm for Normalized Specimen of AISI 4140 Steel in 1N HCl at Room Temperature.

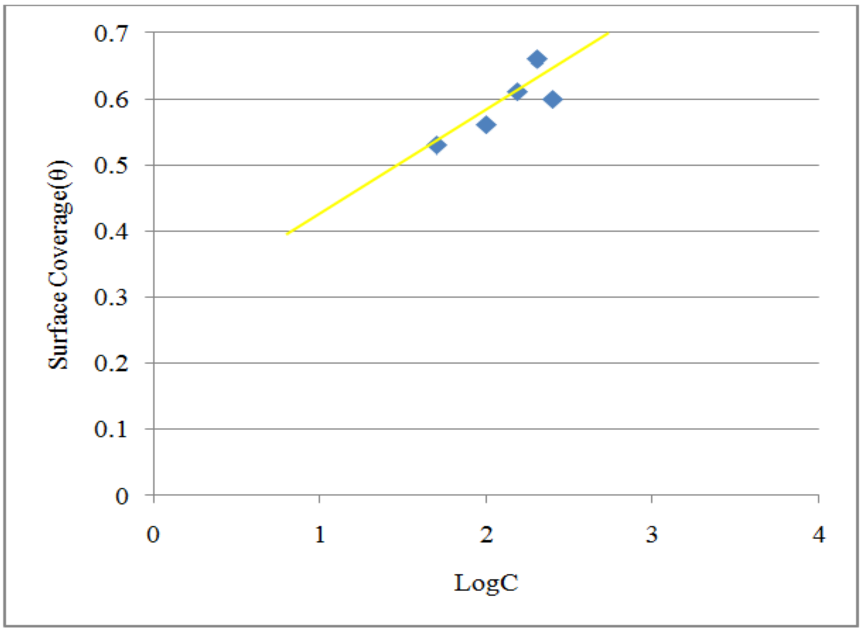

Figure 12: Curve Fitting of Temkins' Adsorption Isotherm for Hardened Specimen of AISI 4140 Steel in 1N HCl at Room Temperature.

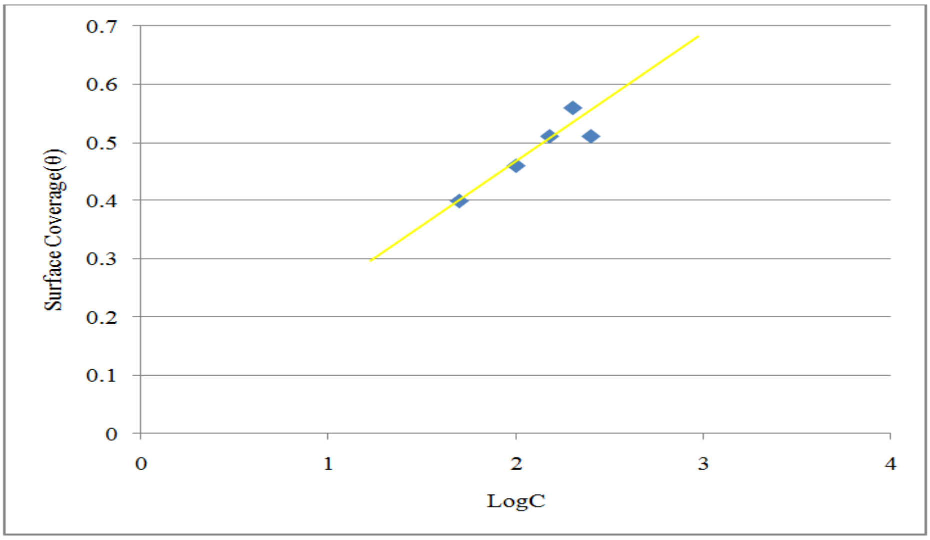

Figure 13: Curve Fitting of Temkins' Adsorption Isotherm for Tempered Specimen of AISI 4140 Steel in 1N HCl at Room Temperature.

- To understand the mechanism of corrosion inhibition, it is necessary to understand the adsorption behavior of organic adsorbents on the metal surface. The surface coverage values (almost) have been graphically tested by switching to various isotherms of adsorption of different concentrations of thiourea from acid solutions.
- The plot of θ versus logC (Figure. 9 – Figure. 13) for various concentrations of thiourea yields a straight line showing that the adsorption of the compound on the steel surface obeys Temkins ' adsorption isotherm.
- The application of Temkins ' adsorption isotherm verifies the principle of monolayer adsorption on a uniform, homogenous metal surface with an adsorption layer interaction. Monolayer adsorption resulted in a reduction in the area available for cathodic and anodic reactions.

4. CONCLUSIONS

- Efficiency of inhibition increases with a increase in concentration of Thiourea up to a critical concentration.
- Thiourea has been found to act predominantly as mixed inhibitor.
- From the tests, it is obvious that there is a marginal impact of heat treatment on AISI 4140 steel's corrosion actions compared to as purchased.
- Inhibition efficiency of thiourea is concentration dependent.
- Adsorption of the compound on the steel surface follows Temkins ' isothermic adsorption and the inhibition is regulated by the physisorption mechanism.

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